XP-001032497 P.D. 29/03/1998 P. 90-91 (2)

Organic and Polymeric Materials for the Fabrications of Thin Film Field-effect Transistors

Zhenan Bao, Andrew J. Lovinger, Ananth Dodabalapur, V. Reddy Raju, and Howard E. Katz

Bell Laboratories, Lucent Technologies, 600 Mountain Avenue, Murray Hill, NJ 07974

Introduction

Organic and polymeric thin-film metal-insulator-semiconductor field-effect transistors (MISFETs) have received increasing interest recently because of their potential applications in low-cost large area flexible displays and low-end data storage such as smart cards.[1,2] Organic materials offer numerous advantages for easy processing (e.g. spin-coating, printing, evaporation), good compatibility with a variety of substrates including flexible plastics, and great opportunities in structural modifications. Very extensive research has been carried out to identify new materials with promising properties, high charge carrier mobility and high current modulation (on/off ratio). Materials with extended π-conjugation, e.g. conjugated oligomers and polymers, have received the most attention. In order for organic MISFETs to be useful for liquid crystal displays, the field-effect mobility should be greater than 0.1 cm^2/Vs and the on/off ratio must be higher than 10^6. In this paper, we will summarize our recent devolopment in the area of thin film transistors.

Experimental

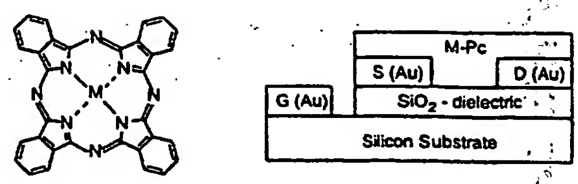
Vacuum deposited devices. The transistor device structure was the same as previously reported.[3] An *n*-doped Si was used as substrate, with gold contact that functioned as the gate and an oxide layer of 3000 Å as the gate dielectric having a capacitance per unit area of 10 nF/cm^2. The channel lengths of the devices were 25, 12, 4, and 1.5 μm. Semiconducting thin films were prepared by vacuum deposition at a rate of 4 to 5 Å/s under a pressure of 2.0×10^{-6} Torr, and the thickness of the resulting films was between 500 to 600 Å. Different substrate temperatures for deposition were obtained by mounting the substrate to a heated copper block controlled by a temperature controller and measured by a thermocouple.

Printed plastic transistors. An ITO-coated poly(ethylene terephthalate) film (from Southwall Technologies) is chosen as the plastic substrate. A polyimide (OPTIMER AL 3046 from Japan Synthetic Rubber Co.) layer is then printed through a screen mask onto the ITO surface. The screen mask is made of a stainless steel fabric with 400 mesh count per inch; an emulsion thickness of about 7.5 μm is used. After being printed, the polyimide dielectric layer is baked at 120° C for an hour. An organic semiconductor layer consisting of regioregular poly(3-alkylthiophene)s (from Aldrich Chemical Co.) with different alkyl chain lengths is then put down by spin-coating, casting, or printing using chloroform as the solvent. Finally, the device is completed by printing the drain and source electrodes using a conductive ink (479SS from Acheson Co.) through a screen mask made of the same fabric and using the same thickness of emulsion. The drain and source electrodes are two strips 0.5 mm x 4 mm each, separated by a gap of 100 μm, and are about 10 μm thick.

The electric characteristics of these devices were measured under vacuum (10^{-3} Torr) unless otherwise specified. The current-voltage characteristics were obtained with a Hewlett-Packard (HP) 4145B analyzer. X-ray diffractiograms were obtained in the reflection geometry using Ni-filtered CuK_{α} radiation. Electron microscopy and diffraction was conducted at 100 kV on C-coated films that had been shadowed with Pt at $\tan^{-1}1/2$ to increase contrast.

Results and Discussion

***P*-channel matrials.** *Vacuum deposited p-channel materials.* Most metallophthalocyanines (MPcs) are commercially available in large quantity and high purity. They are chemically and thermally stable and have been widely used in dye processing, spectral sensitization, chemical sensors, and optical data storage. The semiconducting behavior of metal phthalocyanines was first observed in 1948 and they have since attracted great interest in advancement of prototype organic semiconductors. However, the transistor properties of these compounds have received less attention presumably because of their low reported mobilities (ca. 10^{-4} cm^2/Vs), e.g. in the case of nickel phthalocyanine (Ni-Pc).[4]



M-Pc

M = Cu,Zn,Fe,Sn,Ni,Pt,H_2

(a) (b)

Figure 1. (a) Molecular structure of metallophthalocyanines (M-Pc); (b) Schematic structure of a M-Pc transistor (G, gate; S, source; D, drain).

We have investigated the transistor behavior[1,3] of different metallophthalocyanines (M = Cu,Zn,Pt,Ni,Sn,Fe,H_2). They were found to function as *p*-channel accumulation-mode devices. The charge carrier mobilities of these devices are strongly dependent on the morphology of the semiconducting thin films. Highly ordered films are obtained by vacuum deposition at elevated substrate temperatures. Relatively high mobilities (ca. 0.02 cm^2/Vs for Cu-Pc and greater than 10^{-3} cm^2/Vs for Zn-Pc, Sn-Pc, and H2-Pc) and drain current on/off ratios greater than 10^4 can be achieved with optimized substrate temperature during deposition (T_D).

Soluble p-channel matrials. To truly realize the advantages (i.e. processability and low-cost) of organic materials in device applications, liquid phase processing techniques by spin-coating, casting, or printing are strongly desired. Soluble and processable poly(3-alkylthiophene)s (P3AT) have been found to have many potential applications such as light-emitting diodes, nonlinear optical devices, rechargeable battery electrodes, and field-effect transistors. The 3-alkyl substituents can be incorporated into a polymer chain with two different regioregularities: head-to-tail (HT) and head-to-head (HH). A regiorandom P3AT consists of both HH and HT 3-alkylthiophenes in a random pattern while a regioregular P3AT has only one kind of 3-alkylthiophene, either HH or HT. Regioreular PATs have been shown to have very different properties from their corresponding regiorandom polymers, such as smaller bandgaps, better ordering and crystallinity in their solid states, and substantially improved electroconductivities. We have studied the electrical characteristics of

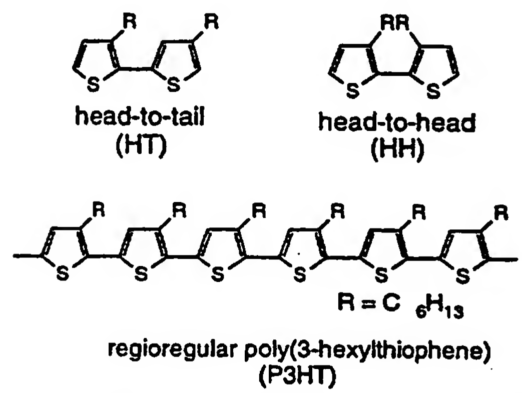


Figure 2. Molecular structure of regioregular poly(3-alkylthiophene)s.

field-effect transistors using solution cast regioregular poly(3-hexylthiophene) (P3HT).[6] We have demonstrated that both high field-effect mobilities (ca. 0.045 cm^2/Vs in the accumulation-mode and 0.01 cm^2/Vs in the depletion-mode), and relatively high on/off current ratios (greater than 10^3) can be achieved. We find that the film quality and field-effect mobility are strongly dependent on the choice of solvents. In addition, treating a film

with ammonia or heating to 100° C under N_2 can increase the on/off ratio without decreasing the mobility.

Printed plastic transistors. With the above liquid phase processable polymer, we have made the first transistor in which all the essential components (electrodes, dielectric, and semiconductor) are printed. We have demonstrated that high performance transistors can be made by printing technique on a plastic substrate. These transistors consist of a polymer dielectric, a semiconducting regioregular poly(3-alkylthiophene), and two silver electrodes, and all of which have been printed on an ITO-coated plastic substrate. The performance of these transistors are comparable to those from Si substrate and SiO_2 dielectric with lithographically defined Au electrodes. The field effect mobilities are in the order of 10^{-2} cm^2/Vs.

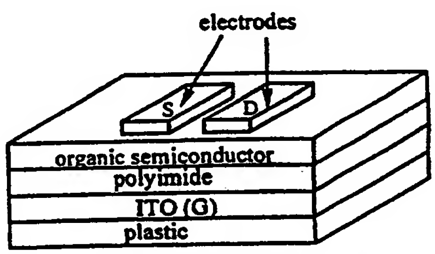


Figure 3. Structure of a printed plastic transistor. S, source; D, drain; G, gate.

Air-stable n-channel matrials. Air-stable *n*-channel semiconducting materials are important components of *p-n* junction diodes, bipolar transistors, and complementary circuits. The existing *n*-channel materials are either very air and moisture-sensitive or have relatively low field-effect mobilities. Recently, we have modified metallophthalocyanines by adding strong electron-withdrawing groups such as -CN, -F, and -Cl to their outer rings. By doing so, the LUMO levels of these molecules are significantly

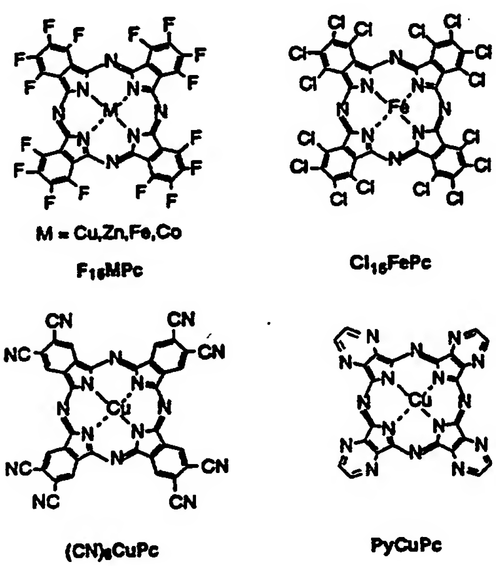


Figure 4. Molecular structures of n-channel semiconductors.

lowered compared to metallophthalocyanines and electron injection and transporting are made possible. Among them, the hexadecafluoro and hexadecachloro metallophthalocyanines were found to function as *n*-channel semiconductors. The best performance has been obtained with Copper hexadecafluoro-phthalocyanine with a field-effect mobility ca. 0.03 cm^2/Vs. We have found that the high mobilities of these compounds are the results of highly ordered films upon vacuum deposition. The charge carrier mobilities of these devices are strongly dependent on the morphology of the semiconducting thin films. Highly ordered films with larger grain sizes, observed by X-ray diffraction and TEM have been obtained by vacuum deposition at elevated substrate temperatures. I have also fabricated a complementary circuit using $F_{16}CuPc$ as the *n*-channel transistor and pentacene as the *p*-channel transistor. In addition, all of the above materials pocess remarkable stability in air and their transistors can be operated both in vacuum and in air. These transistors without any packaging are still functional with high mobilities after stored in open-air for several months. These metallophthalocyanine derivatives are by far the only materials which have been found to have longtime stability in air with mobilites greater than 10^{-2} cm^2/Vs.

Conclusions

New organic and polymeric semiconducting materials with high field-effect mobilities and on/off ratios have been demonstrated. Significant progress has been made in improving the stability of n-channel materials. The demonstration of the first plastic transistor by continuous printing techniques is a promising step towards printed plastic circuits.

Refernces

(1) Katz, H. E. *J. Mater. Chem.* 1997, *7*, 369-376.
(2) Lovinger, A. J.; Rothberg, L. J. *J. Mater. Res.* 1996, *11*, 1581.
(3) Bao, Z.; Lovinger, A. J.; Dobabalapur, A. *Appl. Phys. Lett.* 1996, *69*, 3066-3068.
(4) Guillaud, G.; Simon, J. *Chem. Phys. Lett.* 1994, *219*, 123-126.
(5) Bao, Z.; Lovinger, A. J.; Dodabalapur *Adv. Mater.* 1997, *9*, 42-44.
(6) Bao, Z.; Dodabalapur, A.; Lovinger, A. J. *Appl. Phys. Lett.* 1996, *69*, 4108-4110.
(7) Bao, Z.; Feng, Y.; Dodabalapur, A.; Raju, V. R.; Lovinger, A. J. *Chem. Mater.* 1997, *9*, 1299-1301